

impressions made with this object in view alone. But by the method here adopted, the same plates which are taken for ascertaining the co-ordinates of the stars, serve equally well for measuring their photographic magnitudes. It is perhaps unnecessary to point out that practically the photometric and photographic magnitudes are, for the most part, identical. The remark above will fail of application, if it be possible to determine differences of right ascension and of declination from the traces of the stars with sufficient accuracy.

VI. "On the Development of Voltaic Electricity by Atmospheric Oxidation." By C. R. ALDER WRIGHT, D.Sc., F.R.S., Lecturer on Chemistry and Physics, and C. THOMPSON, F.I.C., F.C.S., Demonstrator of Chemistry, in St. Mary's Hospital Medical School. Received April 17, 1888.

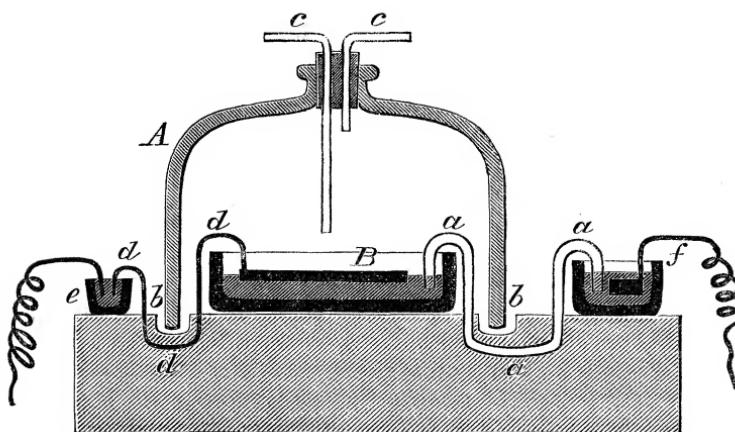
In a preliminary note on this subject ('Roy. Soc. Proc.', vol. 42, p. 212), it has been shown that when copper is immersed in an aqueous solution of ammonia and opposed to an "aeration plate" of some conducting material not otherwise acted upon, lying horizontally on the surface of the fluid, a current flows continuously through a wire, &c., made to connect the two plates, the energy manifested by which is due to the absorption of atmospheric oxygen by the aeration plate and the indirect combination of this with the copper forming cuprous oxide which dissolves in the ammonia. Numerous analogous electromotor cells are readily obtainable by suitably varying the metal susceptible of oxidation and the electrolytic fluid employed, some of which we have submitted to close examination; whilst another class of voltaic cells, acting on much the same principle, we find can be obtained by substituting for the oxidisable metal a platinum or other incorrodible plate immersed in an oxidisable fluid, such as pyrogallol dissolved in caustic soda: preferably the aeration plate is arranged in one vessel on the surface of some convenient fluid (not necessarily identical with the oxidisable one), and the other plate and oxidisable fluid placed in another vessel, the two being connected by a siphon or wet wick; or the whole may be arranged as a gravity battery, the oxidisable fluid being made the heavier one so as to preserve it from direct contact with air; or a U-tube arrangement may be employed. Thus, for example, a platinum plate immersed in an acid solution of ferrous sulphate, or in sulphurous acid solution, connected with a vessel containing dilute sulphuric acid, and an aeration plate of spongy platinum, &c., furnishes an electromotor cell in which the production of a current is accompanied by the virtual transference of oxygen from the aeration plate to the oxidisable fluid, forming

ferric sulphate or sulphuric acid respectively. A considerable enhancement in the E.M.F. of such an arrangement is effected if the oxidisable fluid is rendered *alkaline*, and the aëration plate surrounded by *acid* fluid, as in that case the passage of a current is also accompanied by the mutual neutralisation of the acid and alkali to an extent equivalent to the current flowing (apart from diffusion): the heat of neutralisation of caustic soda and sulphuric acid is (Julius Thomsen) 31,378 gram-degrees, equivalent to 0.675 volt; and similarly in other cases. Thus, tolerably energetic aëration cells are obtained by using caustic soda solution of pyrogallol or sodium hyposulphite (Schützenberger's *hydrosulphite*), and a platinum sponge aëration plate on the surface of diluted sulphuric acid; and somewhat weaker ones if an alkaline solution of ferro-cyanide or sodium plumbate be used, ferri-cyanide or lead dioxide (precipitated in the solid form on the electrode) being the product of the oxidation thus effected, and the E.M.F. being upwards of 0.8 volt in each case.

In all aëration cells, whether oxidisable fluids or metals be employed, one marked feature is the extremely rapid rate at which the E.M.F. of the cell falls if the current generated is made to exceed a very small limiting density relatively to the area of the aëration plate. Of course when this plate is a sheet of polished metal such as platinum foil, this limit lies much lower than when it is a tray of the same area filled with spongy metal, pulverised graphite, &c., because in the latter case the true surface acting is much greater than the actual area of the tray: a number of observations led us to the conclusion that with the most sensitive kinds of aëration plates examined (thin foils or leaves of the precious metals), a measurable depreciation in the E.M.F. of a cell that otherwise would give a constant value, was speedily brought about if made to generate a current of greater density relatively to the aëration plate than about  $\frac{1}{25}$  micro-ampère per square centimetre of surface, or 1 micro-ampère for a plate 5 centimetres square, exposing 25 square centimetres of surface (one side only reckoned); but with aëration plates of spongy metal currents of many times this density produced little or no depreciation even after flowing some time. Even with the most favourable kinds of plates, however, the tendency towards depreciation was so far marked as to render it evident that but little hope could be entertained of utilising the principle of atmospheric oxidation for the production of cheap currents of sufficient power for practical use, excepting when plates of enormous area are employed, so that the density of the current should still be small, even when the current itself was of moderate magnitude. Admitting, however, that a large superficial area (*e.g.*, a lake or artificial reservoir) of fluid were available, and that the cost of a proportionately large system of aëration plates were not prohibitive, it does not seem absolutely impossible

that the production of currents by atmospheric oxidation might be practically effected on the large scale.

We found it difficult to obtain sharp and concordant valuations of the E.M.F. actually set up in cells containing oxidisable fluids, the more so, as the numbers appeared to vary, not only with the nature of the aeration plate and the fluid in contact therewith, but also with the character of the incorrodible plate immersed in the oxidisable fluid, and with the nature and strength of that fluid also. With cells containing oxidisable metals, however, and electrolytic fluids in which the oxides formed were soluble, we found no difficulty in obtaining far more concordant and approximately constant values than would at first sight have appeared likely, or even possible with combinations in which one ingredient was so unstable an element as a film of gaseous matter attracted to the surface of a condensing solid, and simultaneously in contact with a fluid capable of dissolving the gas. Obviously, mechanical disturbances, rapid alterations of temperature, and such like causes would be likely to cause large variations from time to time in the readings of any one particular cell; whilst unavoidable differences in the conditions of surface of otherwise duplicate plates (such as variations in degree of polish, &c.) would render it likely that the average readings of any two duplicate cells would occasionally exhibit considerable divergence; we succeeded, however, in reducing these sources of fluctuations to comparatively small limits, by setting up the cells in an apartment where the temperature varied but little, and only slowly, the readings being mostly taken in the mornings after standing at rest all night; whilst alteration of the fluid by evaporation, attraction of moisture, carbonic acid, &c., from the air, falling in of dust, and so on, was avoided as much as possible by covering over the vessel containing the aeration plate with a bell-jar



A, the siphon connecting this vessel with the other one in which the oxidisable metal was immersed being bent so as to pass under the rim of the jar *a, a, a*. It was found convenient to mount the jar on a block of paraffin wax with a circular groove *b, b*, in which the bell-jar stood, the groove being then filled with mercury so as to make a sort of hydraulic lute; if required, the air inside the jar could be replaced by oxygen, &c., by simply passing in a current of gas through one of a pair of tubes *c, c*, introduced through a perforated cork in the neck of the jar. Usually several aëration plates were separately arranged in the same vessel, each one, B, being connected (by means of a platinum wire *d, d, d*, imbedded in the paraffin wax, passing under the rim of the jar), with a mercury cup *e* outside: in this way the plate of oxidisable metal used, *f*, could be removed at pleasure for cleaning, amalgamating, &c., and replaced without disturbing the aëration plates, and could be opposed at will to any one of these by a simple switch connecting the required mercury cup with the rest of the circuit.

On first setting up such an arrangement and taking readings alternately with any one of the plates opposed to the oxidisable metal, and a Clark's cell, the total resistance in circuit being the same (usually several megohms to reduce the current density sufficiently) values were obtained generally exhibiting progressive alteration (sometimes increase, sometimes decrease) as time elapsed; but after periods varying in different cases from an hour or two to several days, sensibly steady readings were obtained exhibiting little or no variation for days and even weeks together; what variations were observed were generally traceable either to temperature fluctuations or to slight shaking or mechanical disturbance whilst renewing the opposed oxidisable plate, or to slight differences in the latter. If, however, in cells set up with dilute sulphuric acid air had free access, more or less considerable alteration was often brought about after some time through evaporation or attraction of moisture from the air, altering the film of fluid in contact with the aëration plate; and this was still more the case with cells set up with caustic soda solution through absorption of carbonic acid, and with ammonia cells through volatilisation of ammonia.

The result of a large number of observations with cells of various kinds was to show that the following general proposition holds:—

If a cell set up with a given fluid, oxidisable metal, and aëration plate generate an E.M.F. =  $e_1$ , then the effect of substituting another aëration plate for the first is to alter the E.M.F. to  $e_2 = e_1 + K_1$ ; whilst that of substituting a different oxidisable metal is to alter the E.M.F. to  $e_3 = e_1 + K_2$ ; the quantity  $K_1$  being independent of the nature of the oxidisable metal used, but varying with each kind of aëration plate employed, and also to some extent with

the nature of the fluid; and similarly the quantity  $K_2$  being independent of the nature of the aeration plate used, but varying with each kind of oxidisable metal employed, and to some extent also with the nature of the fluid.

For example, in one experiment four aeration plates, respectively platinum sponge, gold sponge, silver sponge, and graphite, were successively opposed, first to amalgamated zinc, and then to brightened lead in a caustic soda solution of strength  $3\cdot45\text{Na}_2\text{O}, 100\text{H}_2\text{O}$ , giving the following average values after making a long series of readings (Clark's cell =  $1\cdot435$  at  $15^\circ\text{C}$ .):—

	Zinc.	Lead.	Difference = $K_2$ .
Platinum sponge.....	1·471	0·769	-0·702
Gold sponge.....	1·435	0·732	-0·703
Silver sponge.....	1·619	0·916	-0·703
Graphite .....	1·400	0·696	-0·704
		Mean..	-0·703

Values of $K_1$ .	Zinc.	Lead.	Mean.
Platinum sponge replaced by gold sponge .....	-0·036	-0·037	-0·0365
Platinum sponge replaced by silver sponge .....	+0·148	+0·147	+0·1475
Platinum sponge replaced by graphite	-0·071	-0·073	-0·072
Gold sponge replaced by silver sponge .....	+0·184	+0·184	+0·184
Gold sponge replaced by graphite...	-0·035	-0·036	-0·0355
Silver sponge replaced by graphite...	-0·219	-0·220	-0·2195

Numerous other experiments of the same kind were made with analogous results in all cases; the values for  $K_1$  and  $K_2$  respectively found in any given set of observations never differing by quantities outside the limits of experimental error. The average values of  $K_1$  or  $K_2$  thus deduced for a given fluid, however, always differed measurably from those similarly deduced for a different fluid, even when that was a similar solution but of different strength. The tables hereafter described illustrate these differences more fully.

*Cells set up with Caustic Soda Solution as Electrolytic Fluid, and various Aëration Plates opposed to Zinc.*

When steadiness was once obtained, we found that the fluctuations observed from day to day in a given cell set up with amalgamated zinc as oxidisable metal (freshly amalgamated each day) rarely exceeded  $\pm 0.003$  to  $0.004$  volt difference from the mean of several days (sometimes some weeks) readings. Duplicate cells, however, gave average readings exhibiting greater differences up to  $\pm 0.025$  or  $\pm 0.030$  volt: thus eighteen different cells set up with platinum-foil or thin leaf, caustic soda solution of strength  $3.45\text{Na}_2\text{O}, 100\text{H}_2\text{O}$ , and amalgamated zinc gave the following results:—

Maximum mean reading of any given cell .....	1.445
Minimum mean reading of any given cell.....	1.403
Average reading of all.....	1.423
Probable error of average .....	$\pm 0.0019$

Even with a much smaller number of cells, the probable error was usually well within  $\pm 0.005$  volt, the differences observed with different cells mainly depending on the unavoidably slight differences in the surface of the metal, &c., constituting the aëration plate.

On substituting a stronger solution of caustic soda for a weaker one, as a rule an increment in average value was observed, and *vice versa*; but the extent of the alteration varied considerably with different kinds of aëration plates: with solutions of strength  $0.05\text{Na}_2\text{O}, 100\text{H}_2\text{O}$  the readings fluctuated so irregularly as to prevent any approach to an accurate average valuation; but with stronger solutions the readings were sufficiently concordant to reduce the probable error of the final average to only  $\pm$  a few millivolts.

*Cells set up with  $3.45\text{Na}_2\text{O}, 100\text{H}_2\text{O}$ .*

Aëration plate.	No. of cells.	Maximum.	Minimum.	Average.
Silver sponge (from acetate) ..	8	1.624	1.615	1.618
Palladium sponge .....	4	1.569	1.549	1.563
Silver sponge (from chloride) ..	4	1.551	1.455	1.484
Platinum sponge.....	14	1.491	1.450	1.463
Palladium foil .....	4	1.468	1.422	1.448
Gold sponge.....	10	1.450	1.433	1.443
Graphite (natural) .....	9	1.465	1.392	1.428
Gold leaf and foil .....	16	1.449	1.402	1.426
Platinum leaf and foil .....	18	1.445	1.403	1.423
Silver leaf and foil.....	21	1.425	1.367	1.396
Carbon, Specimen A .....	4	1.383	1.344	1.365
Carbon, Specimen B .....	4	1.307	1.269	1.287

The spongy metals used were prepared as follows:—Silver sponge (from acetate) by gently igniting in the air crystallised silver acetate; that from chloride by boiling well-washed silver chloride with sugar and caustic soda until reduction was nearly complete. Spongy palladium and platinum by gentle ignition of the ammonio-chlorides of palladium and platinum respectively; and spongy gold by gentle ignition in the air for a long time (so as to burn off carbon) of cinchonine auro-chloride. The graphite was a very pure natural specimen from Ceylon; when used it was coarsely powdered, and spread over the surface of porous earthenware like the spongy metals. As regards the leaves and foils of silver, gold, and platinum, no discernible differences could be distinguished between the values given by the thinnest leaves and comparatively thick foils (up to 0·1 mm. in thickness) in any of the three cases, saving that the latter took a much longer time before steady readings were obtained. Carbon (A) was a piece of electric light rod ground down to a thin flat plate; (B) part of the carbon for a Leclanché cell similarly treated.

It may be noticed that some aeration plates composed of spongy platinum with a top layer of platinum-black (precipitated from the chloride by boiling with caustic soda and alcohol) gave figures pretty close to those furnished by platinum sponge; as also did other plates consisting of porous earthenware painted over with platinochloride of ammonium made into a paste with gum-water, ignited, and the film of spongy platinum left on the surface burnished bright.

	Maximum.	Minimum.	Mean.
Platinum sponge and black.....	1·473	1·441	1·457
Burnished pot .....	1·455	1·453	1·454
Platinum sponge alone .....	1·491	1·450	1·463

When dilute sulphuric acid was the fluid, however, the platinum-black plates gave values upwards of a decivolt *higher* than sponge, and the burnished pots about as much *lower* than sponge.

A large number of observations were made with sets of aeration plates and oxidisable metals in contact with caustic soda solution of one strength subsequently changed for a different one, and so on, only those readings being taken into account when steadiness was attained; thus the following figures were obtained where the plates were read first in  $1\cdot75\text{Na}_2\text{O}, 100\text{H}_2\text{O}$ , then in  $3\cdot45\text{Na}_2\text{O}, 100\text{H}_2\text{O}$ , then in  $7\cdot15\text{Na}_2\text{O}, 100\text{H}_2\text{O}$ , and then in the first again, and so on several times, so that each plate was read several times in each strength of fluid. In all cases the stronger the solution the higher the value, but the effect of a given increment in solution-strength was very different with dif-

ferent aeration plates: thus the following mean readings were obtained.

Increment in E.M.F. brought about by increasing the Strength of Caustic Soda Solution from  $m\text{Na}_2\text{O}, 100\text{H}_2\text{O}$  to  $n\text{Na}_2\text{O}, 100\text{H}_2\text{O}$ .

	$m = 1\cdot75.$ $n = 3\cdot45.$	$m = 3\cdot45.$ $n = 7\cdot15.$	$m = 1\cdot75.$ $n = 7\cdot15.$
Platinum foil.....	0·033	0·015	0·048
Platinum sponge .....	0·029	0·004	0·033
Silver foil .....	0·014	0·032	0·046
Silver sponge.....	0·019	0·027	0·046
Gold foil.....	0·031	0·010	0·041
Gold sponge .....	0·027	0·016	0·043
Palladium foil .....	0·032	0·007	0·039
Graphite .....	0·029	0·001	0·030

Combining these figures with the average values previously obtained for  $3\cdot45\text{Na}_2\text{O}, 100\text{H}_2\text{O}$ , the following mean values result.

E.M.F. of Cells set up with Amalgamated Zinc and  $m\text{Na}_2\text{O}, 100\text{H}_2\text{O}$ .

	$m = 1\cdot75.$	$m = 3\cdot45.$	$m = 7\cdot15.$
Spongy silver (acetate) .....	1·599	1·618	1·645
Spongy palladium.....	..	1·563	..
Spongy silver (chloride) .....	..	1·484	..
Spongy platinum .....	1·334	1·463	1·467
Palladium foil .....	1·416	1·448	1·455
Spongy gold .....	1·416	1·443	1·459
Graphite .....	1·399	1·428	1·429
Gold foil and leaf .....	1·395	1·426	1·436
Platinum foil and leaf.....	1·390	1·423	1·438
Silver foil and leaf .....	1·382	1·396	1·428
Carbon (mean of A and B).....	..	1·326	..

*Cells set up with Caustic Soda Solution and Various Kinds of Aeration Plates opposed to Lead.*

It was found that when a given aeration plate had attained to a condition of steadiness, if opposed to a piece of freshly brightened pure lead, somewhat irregular readings were obtained for a few minutes owing to the effect of the alkali on the polish of the lead; in a short time, however, this disturbing influence mostly subsided, and tolerably constant values were obtained for two or three hours, after which a slight lowering generally began to be noticed con-

currently with a notable increase in the amount of corrosion of the lead; the following values were obtained during this period of two or three hours whilst the readings were comparatively constant.

Values of  $K_2$  = effect of substituting Brightened Lead for Amalgamated Zinc in  $m\text{Na}_2\text{O}, 100\text{H}_2\text{O}$ .

	$m = 1\cdot75.$	$m = 3\cdot45.$	$m = 7\cdot15.$
Maximum.....	-0.690	-0.703	-0.708
Minimum.....	-0.668	-0.681	-0.678
Average.....	-0.678	-0.690	-0.691

E.M.F. of Cells set up with Brightened Lead and  $m\text{Na}_2\text{O}, 100\text{H}_2\text{O}$ .

	$m = 1\cdot75.$	$m = 3\cdot45.$	$m = 7\cdot15.$
Spongy silver (acetate).....	0.921	0.928	0.954
Spongy palladium .....	..	0.873	..
Spongy platinum.....	0.756	0.773	0.776
Palladium foil .....	0.738	0.758	0.764
Spongy gold .....	0.738	0.753	0.768
Graphite .....	0.721	0.738	0.738
Gold foil and lead .....	0.717	0.736	0.745
Platinum foil and lead .....	0.712	0.733	0.747
Silver foil and lead .....	0.704	0.706	0.737
Carbon .....	..	0.636	..

Here, as with cells set up with zinc, the E.M.F. rises with the solution-strength, but not to so great an extent, since the (negative) value of  $K_2$  also increases therewith.

*Cells set up with Dilute Sulphuric Acid and Copper as Oxidisable Metal.*

As a general rule, cells set up with dilute sulphuric acid showed somewhat less steadiness, and wider limits of fluctuation between the mean values of duplicates, than cells containing caustic soda; but the numbers obtained were sufficiently concordant to show that, *ceteris paribus*, the E.M.F. of a copper-sulphuric acid aeration plate cell increases with the solution-strength, and that practically no difference is noticeable between the mean value obtained with the thinnest leaves and foils of the same metals up to 0.1 mm. in thickness.

Mean E.M.F. of Cells set up with Electro-copper and  
 $m\text{H}_2\text{SO}_4, 100\text{H}_2\text{O}$ .

	$m = 2\cdot 5.$	$m = 10.$	Increment with stronger solution.
Platinum sponge covered with platinum black.....	..	0·780	..
Platinum sponge.....	0·636	0·658	0·022
Platinum sponge: thin layer burnished.....	..	0·530	..
Palladium sponge.....	0·517	0·527	0·010
Gold.....	0·496	0·506	0·010
Platinum foil and leaf.....	0·444	0·460	0·016
Palladium foil.....	0·447	0·458	0·011
Gold foil and leaf.....	0·445	0·458	0·013
Graphite.....	0·449	0·456	0·007
Carbon (A).....	..	0·464	..
Carbon (B).....	..	0·446	..
Spongy silver.....	..	About 0·35*	..
Silver foil and leaf.....	..	About 0·25*	..

*Cells Set up with Dilute Sulphuric Acid and Amalgamated Zinc, Bright Cadmium, and Silver Foil, as Oxidisable Metals.*

The value of  $K_2$ , the effect of substituting amalgamated zinc for copper, was found to be generally some 2 to 3·5 centivolts higher at first than after standing awhile; after one or two hours, the zinc plates were generally more or less coated with minute bubbles of hydrogen through local action, and then gave pretty constant readings

Value of  $K_2$  = effect of substituting other Metals for Copper  
in  $m\text{H}_2\text{SO}_4, 100\text{H}_2\text{O}$ .

	Zinc.		Cadmium.		Silver.
	$m = 2\cdot 5.$	$m = 10.$	$m = 2\cdot 5.$	$m = 10.$	$m = 10.$
Maximum.....	+1·054	+0·978	+0·731	+0·742	-0·29
Minimum.....	+1·033	+0·962	+0·705	+0·709	-0·12
Average .....	+1·045	+0·970	+0·720	+0·725	Abt. -0·20

\* The values obtained with silver aeration plates of all kinds were most irregular and wanting in steadiness; with spongy silver (both from acetate and from chloride) numbers were obtained varying between 0·28 and 0·43, in the majority of cases not far from 0·34 to 0·36; and with foil and leaf, numbers lying between 0·17 and 0·36.

for some hours longer; the following figures refer to this latter period when nearly constant but lower values were obtained. Cadmium did not alter so markedly on standing; silver gave very irregular values.

E.M.F. of Cells set up with Amalgamated Zinc, Brightened Cadmium, and Pure Silver Foil in  $mH_2SO_4, 100H_2O$ .

	Zinc.		Cadmium.		Silver.
	$m = 2.5.$	$m = 10.$	$m = 2.5.$	$m = 10.$	$m = 10.$
Platinum sponge coated with platinum black.	..	1.750	..	1.505	About 0.58
Platinum sponge.....	1.681	1.628	1.356	1.383	„ 0.46
Palladium sponge.....	1.562	1.497	1.237	1.252	„ 0.33
Gold sponge .....	1.541	1.476	1.216	1.231	„ 0.31
Platinum foil and leaf.	1.489	1.430	1.164	1.185	„ 0.26
Palladium foil.....	1.492	1.428	1.167	1.183	„ 0.26
Gold foil and leaf.....	1.490	1.428	1.165	1.183	„ 0.26
Graphite .....	1.494	1.426	1.169	1.181	„ 0.255
Carbon (mean of A and B).....	..	1.425	..	1.180	..

In the case of the cadmium cells, the E.M.F. rises with the solution-strength as it does in the copper cells, and more rapidly because  $K_2$  is positive and also rises; but in the case of the zinc cells, the E.M.F. falls as the solution-strength rises, because  $K_2$  is here much smaller with the stronger solution.

*Cells Set up with Ammoniacal Solutions as Electrolytic Fluids, and Electro-copper as Oxidisable Metal.*

It was found impossible to keep any one cell of this kind under anything like constant conditions as regards the nature of the fluid on account of the loss of ammonia, experienced to a large extent even when covered with a jar, &c.; accordingly, the following values can only be regarded as approximate, especially in the case of the stronger solutions. The strength of the fluid was ascertained by sampling and analysis from time to time, and consequently interpolation was sometimes requisite in order to reduce the values obtained with different sets of plates to the same mean strength. On the whole, however, the figures indicate that with solutions of pure ammonia, the E.M.F. rises with the strength of the solution; and similarly with liquids containing sal-ammoniac as well.

E.M.F. of Cells set up with Electro-copper and Ammoniacal Solutions,  $x\text{NH}_3, y\text{NH}_4\text{Cl}, 100\text{H}_2\text{O}$ .

	$y = 0$ (pure ammonia).			$y = 0\cdot8.$	$y = 5.$	
	$x = 1\cdot25.$	$x = 2\cdot0.$	$x = 2\cdot6.$	$x = 2\cdot6.$	$x = 2\cdot6.$	$x = 12.$
Spongy platinum.	0·440	0·460	0·470	0·552	0·579	..
Spongy gold .....	0·410	0·450	0·460	0·492	0·522	..
Spongy silver .....	0·395	0·410	0·420	..	0·471	..
Carbon (A) .....	..	..	..	..	0·470	0·570
Palladium foil .....	..	..	..	..	0·450	0·560
Platinum foil .....	0·395	0·405	0·410	0·437	0·450	0·520
Graphite .....	0·330	0·340	0·355	0·404	0·445	0·510
Gold foil .....	..	..	..	..	0·403	..
Silver .....	..	..	..	..	0·403	..

With brine saturated with ammonia and spongy platinum aëration plates higher values still were obtained, reaching up to about 0·75 as a maximum; but, owing to evaporation of ammonia, these high values rapidly diminished on standing a short time.

*Cells set up with Amalgamated Zinc and Bright Silver Foil as Oxidisable Metals.*

The following numbers were obtained as the average values for cells of this kind :—

Values of  $K_2$  = effect of substituting other Metals for Copper in  $x\text{NH}_3, y\text{NH}_4\text{Cl}, 100\text{H}_2\text{O}$ .

$x = 2\cdot6.$

	$y = 0$ (pure ammonia).	$y = 0\cdot8.$	$y = 5.$
Amalgamated zinc .....	+ 0·960	+ 0·930	+ 0·920
Bright silver .....	- 0·385	- 0·340	- 0·340

E.M.F. of Cells set up with Amalgamated Zinc or Bright Silver and Ammoniacal Solutions,  $x\text{NH}_3, y\text{NH}_4\text{Cl}, 100\text{H}_2\text{O}$ .

$$x = 2.6.$$

	Zinc.			Silver.		
	$y = 0.$	$y = 0.8.$	$y = 5.$	$y = 0.$	$y = 0.8.$	$y = 5.$
Platinum sponge	1.430	1.482	1.499	0.085	0.212	0.239
Gold sponge ...	1.420	1.422	1.442	0.075	0.152	0.182
Silver sponge ...	1.380	..	1.391	0.035	..	0.131
Platinum foil ..	1.370	1.367	1.370	0.025	0.097	0.110
Graphite .....	1.315	1.334	1.365	..	0.064	0.105

In general the E.M.F. rises with increased solution-strength, platinum foil being exceptional when opposed to zinc, the E.M.F. here being practically constant.

The various tables above stated clearly show that the order of magnitude of the E.M.F. generated when a given kind of aeration plate is opposed to a given oxidisable metal, depends on the nature, and to some extent also on the strength, of the solution used as electrolytic fluid. The following table indicates the relative order in which various plates come in solutions of caustic soda, sulphuric acid, and ammoniacal liquors respectively:—

<i>Caustic Soda.</i>	<i>Sulphuric Acid.</i>	<i>Ammoniacal Fluids.</i>
Silver sponge (acetate).	Platinum black.	Platinum sponge.
Palladium sponge.	Platinum sponge.	Gold sponge.
Silver sponge (chloride).	Palladium sponge.	{ Silver sponge.
{ Platinum sponge.	Gold sponge.	{ Carbon.
{ Platinum black.	Platinum foil and leaf.	{ Palladium foil.
{ Palladium foil.	Palladium foil.	{ Platinum foil
{ Gold sponge.	Gold foil and leaf.	Graphite.
{ Graphite.	Graphite.	{ Gold foil.
{ Gold foil and leaf.	Carbon.	{ Silver foil.
{ Platinum foil and leaf.	Silver sponge.	
Silver foil and leaf.	Silver foil and leaf.	
Carbon.		

In all cases a metal in the state of sponge gives a higher value than when in the state of polished foil or thin leaf.

*Comparison between the E.M.F. generated in Aeration Plate Cells and the Chemical Action going on therein.*

In the case of cells with caustic soda as electrolytic fluid, the nett chemical change is the oxidation of the oxidisable metal to form

oxide (or hydroxide) which in the case of zinc and lead further dissolves in the alkaline liquid forming zincate or plumbate; the heat of solution of zinc and lead oxides in caustic soda being unknown, the total heat development cannot be exactly calculated. According to Julius Thomsen,  $Zn_2O = 85430$ , and  $Pb_2O = 50300$  gram-degrees, corresponding with the E.M.F.'s. 1.837 and 1.081 respectively,\* wherefore the E.M.F. due to the chemical action (including formation of zincate and plumbate) must be higher still; on the other hand, the highest values observed in any aeration cell were only 1.645 and 0.954 respectively (spongy silver-acetate), whilst values of from 1 to 4 decivolts lower still were observed with other plates. Hence *the E.M.F. actually generated in these cells falls very considerably short of that corresponding with the chemical change*, even under the most favourable circumstances, *i.e.*, when producing only an infinitesimal current; whilst when producing a somewhat greater current, but still of only small density (not exceeding a fraction of a micro-ampère per square centimetre of aeration plate surface in some cases), running down and marked depreciation of E.M.F. is rapidly brought about.

Much the same remarks apply to cells set up with sulphuric acid and with ammoniacal fluids; in the former the nett chemical change is the oxidation of the metal and solution of the oxide in the acid forming the sulphate. Julius Thomsen gives the heat values—

Zinc . . . . .	$Zn_2O, SO_3aq$	= 106090	gram-degrees	= 2.281	volts.
Cadmium . . .	$Cd_2O, SO_3aq$	= 89500	"	= 1.924	"
Copper . . . . .	$Cu_2O, SO_3aq$	= 55960	"	= 1.203	"
Silver . . . . .	$Ag_2O, SO_3aq$	= 20390	"	= 0.438	"

Whilst the highest observed values in the case of the first three metals *fall short of these by 4 to 5 decivolts*, and with less active aeration plates the deficiency is much greater. Silver, however, when employed as oxidisable metal, does not show this falling off, but rather the reverse, the highest value observed (platinum black) being about 0.58, and the next highest (platinum sponge) about 0.46, both exceeding the E.M.F. calculated from the heat value; obviously this is due, not to anything connected with the aeration plates, but rather to the large negative value of the thermo-voltaic constant† pertaining to silver in contact with sulphuric acid, evidenced also by the circumstance observed by us, that when silver is substituted for zinc in a Grove's cell, instead of the E.M.F. being depressed by an amount

\* Taking  $J = 41.5 \times 10^6$ , and the unit C.G.S. current as evolving  $0.0001036$  gram of hydrogen per second, whence the factor for converting gram-degrees into volts is sensibly  $4300 \times 10^{-8} = 0.000043$  per gram-equivalent.

† 'Phil. Mag.', vol. 19, 1885, pp. 1 and 102.

corresponding with the difference in heat of formation of zinc and silver sulphates (85700 gram-degrees = 1.843 volts) it is only depressed by an amount short of this by some 5 or 6 decivolts. Similarly in the ammoniacal cells where (as in the caustic soda cells) the action consists in the oxidation of a metal and the solution of the oxide formed in the ammoniacal liquor, Julius Thomsen gives the heat values—

$$\begin{array}{ll} \text{Zinc} \dots \dots \dots & \text{Zn}_2\text{O} = 85430 = 1.837 \text{ volt.} \\ \text{Copper} \dots \dots \dots & \text{Cu}_2\text{O} = 40810 = 0.877 \text{ ,} \\ \text{Silver} \dots \dots \dots & \text{Ag}_2\text{O} = 5900 = 0.127 \text{ ,} \end{array}$$

Whence the E.M.F. corresponding with the total chemical change must somewhat exceed these amounts by the quantity representing the respective heats of solution in ammonia liquor of the metallic oxides: the highest values observed with zinc and copper *fall distinctly short of these amounts*, whilst the numbers obtained with many kinds of aëration plates in weaker solutions exhibit a large deficiency; on the other hand, cells containing silver as oxidisable metal show no large falling off, and in the case of the highest values an actual *excess* of E.M.F., again indicating a somewhat large negative value for the thermo-voltaic constant applicable to silver in contact with ammoniacal fluids.

It is noticeable that the values of  $K_2$  deduced above are not widely different from those equivalent to the difference in heat of oxidation of the various metals, silver excepted: thus with the caustic soda cells—

$$\left. \begin{array}{l} \text{Zn}_2\text{O} = 85430 \\ \text{Pb}_2\text{O} = 50300 \end{array} \right\} \text{Difference } -35130 = -0.755 \text{ volts.}$$

Observed values. .... from -0.678 to -0.691.

With the sulphuric acid cells the differences between the heat of formation of copper sulphate, and that of zinc, cadmium, and silver sulphates respectively, are +50130, +33540, and -35570, corresponding with—

<i>Volts.</i>	<i>Observed values of <math>K_2</math>.</i>
Copper replaced by zinc = +1.078	+0.970 to +1.054
Copper replaced by cadmium = +0.721	+0.720 to +0.725
Copper replaced by silver = -0.765	About -0.020

With the ammoniacal cells the differences between the heat of formation of cuprous oxide and of zinc and silver oxides respectively are +44620, and -34910, corresponding with—

Volts.	Observed values of $K_2$ .
Copper replaced by zinc = +0.960	+0.920 to +0.960
Copper replaced by silver = -0.750	-0.340 to -0.385

Whilst with zinc, lead, copper, and cadmium, the observed values of  $K_2$  in no case differ very widely from those equivalent to the differences in heat of formation, those observed with silver show large differences, indicating as before that silver exhibits a high negative value for its thermo-voltaic constant in each case, viz., -0.5 to -0.6 in contact with dilute sulphuric acid, and near to -0.4 in contact with ammoniacal fluids, this latter value being close to those found previously for silver in contact with neutral solutions of its sulphate, nitrate, and acetate (*loc. cit.*).

On the whole, except when an oxidisable metal is used exhibiting a high negative value for its thermo-voltaic constant, the E.M.F. of a cell containing an aeration plate and an oxidisable metal always falls short, and sometimes largely short, of that equivalent to the chemical changes going on therein even under the most favourable conditions when generating only an infinitesimal current, the deficiency being still more marked when the current density is not so minute: in other words, the *modus operandi* of cells of this class is such as necessarily to render a large fraction of the energy non-adjuvant so far as current is concerned. Just the same remarks apply, as far as our experiments have gone, to cells in which the oxidisable substance is in solution, an extreme case of which is exhibited by cells set up with a solution of sulphurous acid and a submerged platinum foil plate, opposed to an aeration plate of platinum sponge on the surface of dilute sulphuric acid. Such cells give an E.M.F. (when generating only extremely small currents) of from 0.2 to 0.3 volt, whilst the heat of oxidation of sulphurous acid solution,  $\text{SO}_2\text{aq}, \text{O}_2$  is 63634 gram-degrees, according to Julius Thomsen, corresponding with 1.368 volt, or upwards of a volt more than that actually produced.\* Analogous diminutions in E.M.F. are brought about in many other cases, to extents depending not only on the nature of the aeration plate but also on that of the oxidisable fluid.

\* A large part of the depreciation in this case is due to the fact that sulphurous acid solution and platinum constitute an oxidisable portion of a cell behaving as magnesium and aluminium do in cells where they replace zinc, *i.e.*, giving a much smaller E.M.F. than that due to the heat corresponding with the chemical change: thus, if a cell be set up with zinc or dilute sulphuric acid opposed to platinum in sulphuric chromic acid solution, and the zinc and sulphuric acid be then replaced by platinum and sulphurous acid solution, the E.M.F. falls by an amount greater by 0.45 to 0.5 volt than that corresponding with the differences in heat evolution between  $\text{Zn}, \text{O}, \text{SO}_2\text{aq}$  and  $\text{SO}_2\text{aq}, \text{O}_2$  (*viz.*, 106090 - 63634 = 42456 gram-degrees = 0.913 volt): and similarly with other oxidising fluids. Solutions of alkaline sulphites behave similarly.

*Effect of Substituting Oxygen for Air.*

In order to see if any material improvement in the E.M.F. of aeration cells could be effected by substituting tolerably pure oxygen for atmospheric air, we carried out a number of observations with plates under a bell-jar supplied with purified oxygen from a reservoir by means of tubes passing through a cork in the narrow mouth. Readings were first taken for a few days with ordinary air in the jar; oxygen was then admitted and passed through till gradually all air was displaced, and after a day or two when the readings had become constant another series of readings for some days was taken. The oxygen was then displaced by air and another series taken, and so on alternately several times. The following average values were ultimately obtained showing a small, though decided, increment in E.M.F. when atmospheric air was replaced by oxygen.

## Increment in E.M.F. in Oxygen.

	Caustic soda, $7 \cdot 15\text{Na}_2\text{O}, 100\text{H}_2\text{O}$ .	Sulphuric acid, $10\text{H}_2\text{SO}_4, 100\text{H}_2\text{O}$ .
Platinum sponge .....	0·016	0·028
Platinum foil.....	0·012	0·001
Gold sponge .....	..	0·032
Gold foil .....	0·012	0·002
Palladium sponge .....	..	0·033
Palladium foil .....	0·013	..
Silver sponge .....	0·016	..
Silver foil .....	0·016	..
Graphite .....	0·015	0·002

*Aeration Plates in Contact with Oxidisable Atmospheres.*

Some analogous experiments were made with aeration plates in contact with an oxidisable atmosphere (hydrogen or coal-gas), and an electrolytic fluid united by means of a siphon with an external vessel containing an oxidising solution (alkaline permanganate, sulphuric acid containing chromic acid, nitric acid, &c.) in which a plate of platinum foil was immersed. The readings thus obtained were nothing like as concordant as those above described (probably from the difficulty of excluding air completely), showing a tendency to rise continually. The following readings were obtained after several days when the rise had either ceased or greatly slackened in most cases; little difference was observed whether pure hydrogen or coal-gas was used.

A. Cells set up with  $7 \cdot 15\text{Na}_2\text{O}, 100\text{H}_2\text{O}$  in contact with the aeration plates, opposed to platinum foil immersed in a solution of the same

strength shaken up with powdered potassium permanganate to saturation.

B. Cells set up with  $10\text{H}_2\text{SO}_4, 100\text{H}_2\text{O}$  in contact with the aëration plates opposed to platinum immersed in the same liquid after agitation with chromic anhydride to saturation.

	A. Alkaline cells.		B. Acid cells.	
	Hydrogen.	Coal-gas.	Hydrogen.	Coal-gas.
Platinum sponge .....	1.525	1.10	1.02	1.10
Platinum foil .....	0.865	0.85	0.89	0.895
Silver sponge .....	0.422	0.425	..	..
Silver foil .....	0.73	0.78	..	..
Gold sponge .....	..	..	0.845	0.85
Gold foil .....	0.72	0.75	0.87	0.90
Palladium sponge .....	..	..	1.37	1.37
Palladium foil .....	0.87	0.81	0.89	1.12
Graphite .....	0.845	0.83	0.85	0.85

In making these observations currents were used, the density of which in no case exceeded 0.02 micro-ampère per square centimetre of aëration plate surface.

Spongy platinum and palladium obviously are far more effective as regards the E.M.F. set up than the other plates used; the chemical action taking place may be regarded as the decomposition of alkaline permanganate into hydrated manganese dioxide, caustic potash, and oxygen (or of chromic anhydride and sulphuric acid into chromium sulphate, water, and oxygen), and the combination of hydrogen with the oxygen thus set free; according to Thomsen's values, the heat developed would accordingly be per 16 grams oxygen evolved—

	Alkaline cells.	Acid cells.
Decomposition of oxidising agent..	$\frac{1}{3} \times 28355 = 9452$	$\frac{1}{3} \times 30407 = 10136$
Oxidation of hydrogen .....	$= 68360$	$68360$
	<hr/>	<hr/>
	77812	78496
Corresponding with volts.....	$= 1.673$	$1.688$

Hence, even with the most effective plates, the E.M.F. actually generated falls distinctly short of that corresponding with the heat of chemical change. On making the current passing larger by diminishing the external resistance, the E.M.F. always fell rapidly; so that in order to obtain a current capable of producing any considerable

amount of electrolytic decomposition in a voltameter, it was practically impossible to have an acting E.M.F. as high as 1 volt, even with tolerably large platinum sponge plates.

Much the same result was obtained on opposing to one another two platinum sponge aëration plates, one in an atmosphere of hydrogen or coal-gas, the other in contact with air; in no case could any current capable of depositing a few milligrams of silver per day be obtained with an E.M.F. as great as 1 volt; *i.e.*, a total depreciation of upwards of 0.5 volt was occasioned, or more than one-third of the energy due to the chemical change, *viz.*, oxidation of hydrogen to water, representing 68360 gram-degrees, or 1.470 volt. The economical production of currents by the direct oxidation of combustible gases, therefore, does not seem at present to be a problem likely to be readily solved.

The Society then adjourned over Ascension Day to Thursday, May 17th.

*Presents, May 3, 1888.*

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